ELECTROANALYTICAL METHODOLOGY FOR THE DETERMINATION OF ELECTROACTIVE SPECIES USING CHEMICALLY MODIFIED CARBON PASTE ELECTRODE

Final Synopsis of the Thesis submitted

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Introduction

The organic and inorganic compounds or molecules may possess with free ions, lone pair electrons, electrically polarized, multiple bonds or with ionizable groups which has tendency to go either oxidation or reduction or both. Then these organic and inorganic compounds or molecules said to be “Electroactive” or “Electrochemical active” molecules or compounds. These features have put forth the researchers to study on its quantification. It is necessary to have a strict regulation in monitoring the electroactive species concentration which may cause imbalance in the environment and biological health [1-3].

So in order to recognize and quantify the electroactive species various methods and techniques have implemented like chromatographic techniques such as capillary electrophoresis, High performance liquid chromatography, gas chromatography and ion exchange chromatography, electrochemiluminescence, fluorometry, chemiluminescence, spectroscopic methods like spectrofluorometry, liquid chromatography-mass spectrometry, Raman or surface plasmon resonance, etc., immunological assay based [4-9] and electrochemical method. Even though majority of these techniques displays accurate results with remarkable sensitivity, electrochemical method has taken into account for its splendid various reasons. Likewise, it is inexpensive, requires little amount of solvents, easily operated without any difficulties, rapid recognition and does not require more time for sample preparation as compared to other methods [10-12]. It is also significant device in studying the chemical systems. Compared to chemical reactions electrochemical reactions are clean. Under physiological status it is appropriate in determining lower concentrations of electroactive species. These features are major responsible for strengthening the sensitivity and selectivity of the electrode towards the electroactive species. The chief focus in electrochemical methods is related to the voltammetric studies like cyclic voltammetry (CV) and differential pulse voltammetry (DPV). These methods help in achieving

the redox behavior of the target compound and in this manner the kinetics of the reaction mechanism, number of electrons and protons involved in the reaction, production of any unstable intermediate, types of the product formed and detection of any trace level of impurities or metal ions etc., can be studied [13-16].

The nature of all the electrochemical reaction phenomenon are heterogeneous, taking place at the interfacial zone either in a solution or immobilized at the surface of the sensors. While an individual utilize few amount of material for the surface of sensor, This electrode surface has coarseness, their active sites are blocked by adsorbed materials and the types of functional groups present mainly oxides at the electrode surface are major responsible to affect the kinetics of heterogeneous reaction [17]. To overcome from this crisis the electrodes are chemically modified. In depth to chemically modified electrodes (CME's) is an approach to increase the analytical features of the electrode in electrochemical determination. This gives better results in knowing about the charge transfer of the reaction. These electrodes reduce over voltage, lower the background current, and produce augmented current peaks, highly stable and antifouling [18-20]. This also has the ability to quantify the trace levels of electroactive compounds in real sample analysis and also has the tendency to overcome the overlapping of the signals for detecting the electroactive species simultaneously. Modified electrodes can be developed by various methodologies like polymer-coated, electropolymerization, covalently attached, immobilization of surfactants and functionalized.

Carbon materials like graphite flakes, graphene, multiwalled carbon nanotubes, carbon composites etc., were preferred for the electrode material. As an electrochemical sensor they are fairly inexpensive, eco-friendly, substantially conducting with broad potential area, stable in chemically, mechanically, electrically and thermally, good porosity, low IR impedance,

biocompatible, in a control nature the stable layers of modifiers can be attached to the surface. With a suitable binder liquid with insulating aspect the carbon material powder was mixed with précised proportion to form the paste called carbon paste and packed into an electrode body representing carbon paste electrode (CPE). These electrodes are also belonging to heterogeneous electrodes. For better results the CPE's are modified for the electrochemical behavior of electroactive species. In this work the electrochemical response of some electroactive compounds at modified carbon paste electrodes by electropolymerization and surfactant immobilization using voltammetric method was studied.

Summary of the Thesis

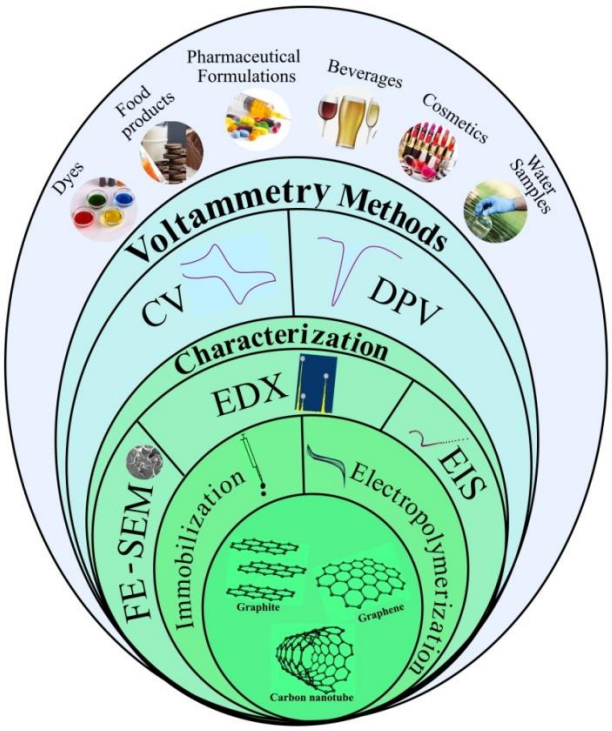
This thesis is enclosed with the research work focused on the electrochemical investigation of electroactive compounds by chemically modified carbon paste electrodes and its application on real sample analysis in cost-effective way. This thesis also illustrates the modification method of carbon paste electrodes like graphite paste electrode, carbon nanotube paste electrode, graphene paste electrode, composite electrodes. The few electroactive organic molecules like Dopamine (DA), Anthrone (ANT), L-Tyrosine (L-TYR), L-Tryptophan (TRP), Riboflavin (RF), Indigo carmine (IC), Catechol (CC) and Vanillin (VLN) were detected by chemically modified carbon paste electrode by voltammetric technique. Further, the following features like reaction mechanism, kinetics of the mechanism, number of electrons engaged in the reaction, sensitivity and selectivity were discussed. The surface characterization of the developed electrodes was also discussed using field emission scanning electron microscopy (FE-SEM). The application of proposed electrode was also discussed in this thesis.

Framework of the Thesis

The thesis entitled with "Electroanalytical Methodology for the Determination of Electroactive Species using Chemically Modified Carbon Paste Electrode" is divided into 10 chapters.

Chapter 1: Introduction to the Role of Electrochemical Sensors and Voltammetry Techniques for the Analysis of Electroactive Molecules

This chapter includes about electroactive molecules and electrochemical sensor's role of electrochemical methods and electrochemical sensor for the analysis of electroactive molecules, electrode substrate material. This section also discusses about cyclic voltammetry and its basic theoretical attributes, DPV, electrodes and EIS. In this section the information about the literature review of voltammetric approaches of various electroactive compounds at various electrodes, objectives and scope of the current work is been discussed.



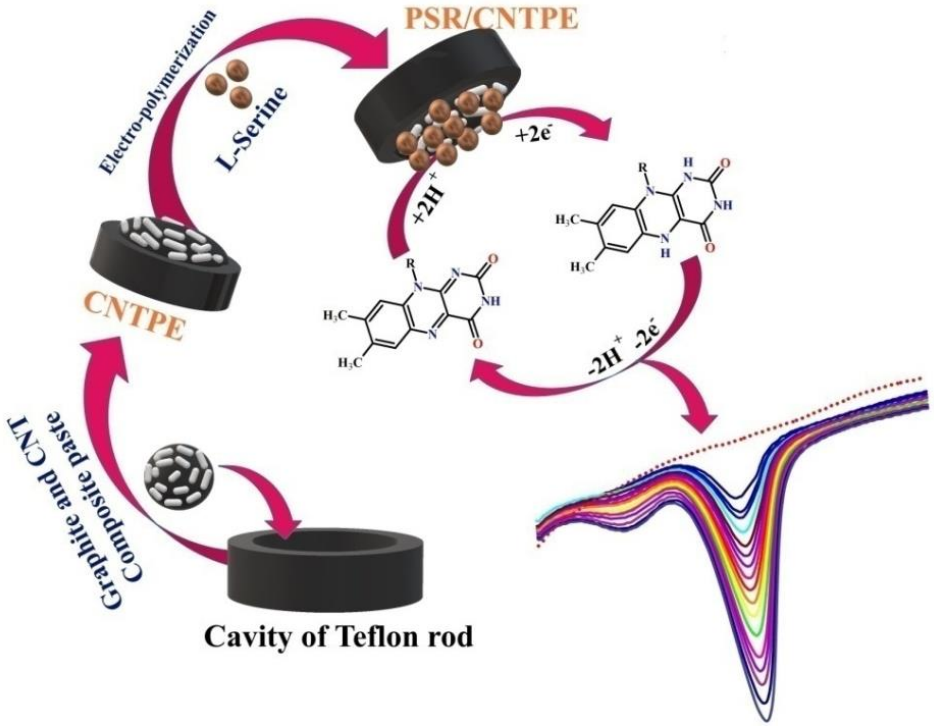
Chapter 2: Experimental

This chapter gives the account of experimental apparatus, its setup and materials employed for the experimental work. The procedure followed for the electrode process and its modification is also been discussed here.

Chapter 3: Mechanistic Insights into the Voltammetric Determination of Riboflavin at Poly (Serine) Modified Graphite and Carbon Nanotube Composite Paste electrode

(**ChemistrySelect,** 6, 2021, 10746-10757. **IF: 2.3**)

Intense present work is directed on the fabrication and application of Poly (serine) modified graphite carbon nanotube composite paste electrode (PSR/CNTPE) for determining the Riboflavin (RF). The surface qualities of the projected sensor were observed by FE-SEM and the conductivity by EIS method. The electrochemical redox activity of the PSR/CNTPE to RF was investigated through Cyclic CV and DPV. Outcomes displays that Poly (serine) in CNTPE enhanced the catalytic performance of the electrode towards the redox reaction of RF. The voltammetric response of PSR/CNTPE exhibited linear dependence for extended concentration range of RF from 6 μM to 50 μM with lower detection limit of 3.4×10^{-8} M. The PSR/CNTPE revealed to be reproducible, highly stable and successfully validated for the pharmaceutical, beverage and milk samples. The fabricated electrode was conducive and displayed two well-separated oxidation signals for the solution containing two vitamins RF and Folic Acid (FA). The projected sensor is an adequate candidate for electrochemical sensing of RF.

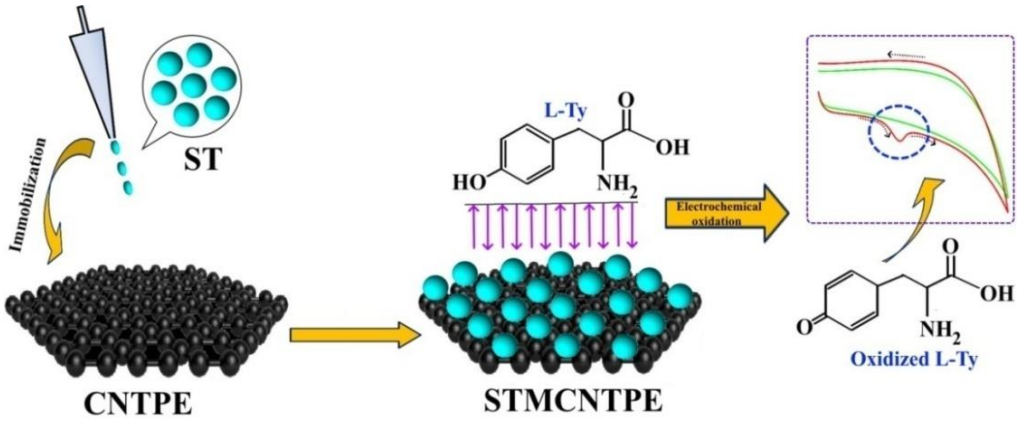


Chapter 4: Electrochemical validation of L-Tyrosine with Dopamine using composite surfactant modified carbon nanotube electrode

(**Journal of Iranian Chemical Society,** 18, 2021, 3493-3503. **IF: 2.27**)

This chapter illustrates the novel work about Sodium lauryl sulphate and Triton X- 100 composite surfactant immobilized on the carbon nanotube paste electrode (STMCNTPE) as electrochemical sensor for the electro-catalytic oxidation of L-Tyrosine (L-TYR) and Dopamine (DA) through CV. The STMCNTPE exhibited a robust enhancement impact on the oxidation of L-TYR with enhanced current signal compared to other electrodes. In ideal conditions, various parameters were studied such as pH value, concentrations of surfactants, different range of Sweep rates, the concentration of an analyte, simultaneous study and the interference analysis. The proposed sensing film unveiled with detection limit 3.75 $\times 10^{-7}$ M and quantification limit

1.22 $\times 10^{-6}$ M for wide linear range. The STMCNTPE revealed with remarkable sensitivity, selectivity, long-term stability, good reproducibility and repeatability, biocompatible, enhanced electrode fouling resistance, and anti-interference. Finally, the sensing film STMCNTPE carried out successfully for the analysis of L-TYR in cow's milk and pharmaceutical drug.

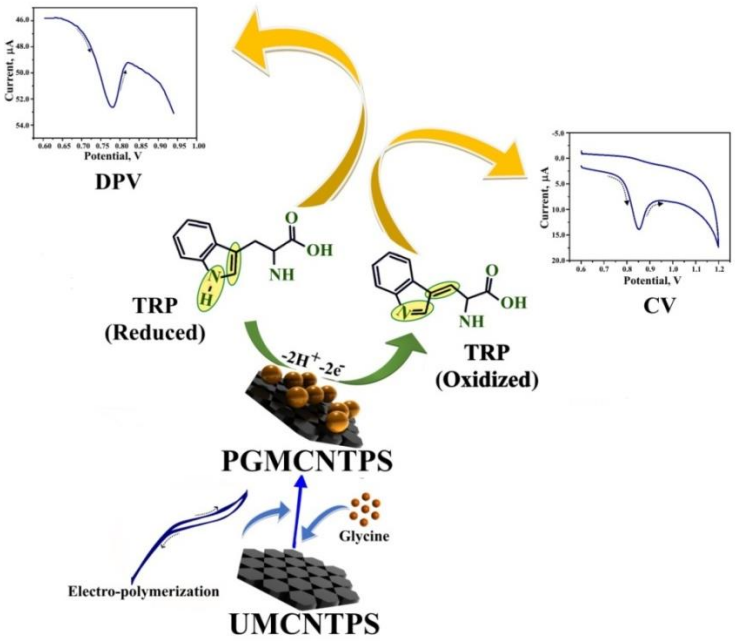


Chapter 5A: Electrochemical Behaviour and Voltammetric Analysis of L-Tryptophan at Highly sensitive Poly – (Glycine) Modified Carbon Nanotube Paste Sensor

(**Materials Research Innovations,** 26, 2022, 134-143. **Cite Score: 4.0**)

L-Tryptophan (TRP) displays a significant role in biotic life as it has various pharmacological activities. In the present work, we developed Poly-(Glycine) modified carbon nanotube paste electrode (PGMCNTPE) as a biosensor for eliciting the electro-catalytic oxidation of TRP. The surface of the sensors was characterized by FE-SEM and EIS. The analysis of TRP was succeeded at the surface of PGMCNTPE for their high electrical conductivity and electrostatic forces that amplified the oxidation peak current by 8 fold in CV and by 12 fold in DPV. The activity of sensor on TRP was manifested to be irreversible reaction proceeding with the transfer of $2e^-$ and $2H^+$ and adsorption controlled. Crucial parameters likely, pH, sweep rate and the

number of cycles of modifiers for modification of electrode were optimized and encouraged in evaluating sensitivity for quantitative analysis by differential pulse voltammetry. Under the optimal state, it was noteworthy that the execution of the sensor revealed to have a low detection limit of 0.42 μM on a broad linear range of 20 μM to 100 μM. The stability, repeatability, and reproducibility of PGMCNTPS were estimated. Lastly, the viability of the fabricated sensor in the determination of TRP was exploited successfully in the pharmaceutical supplement.

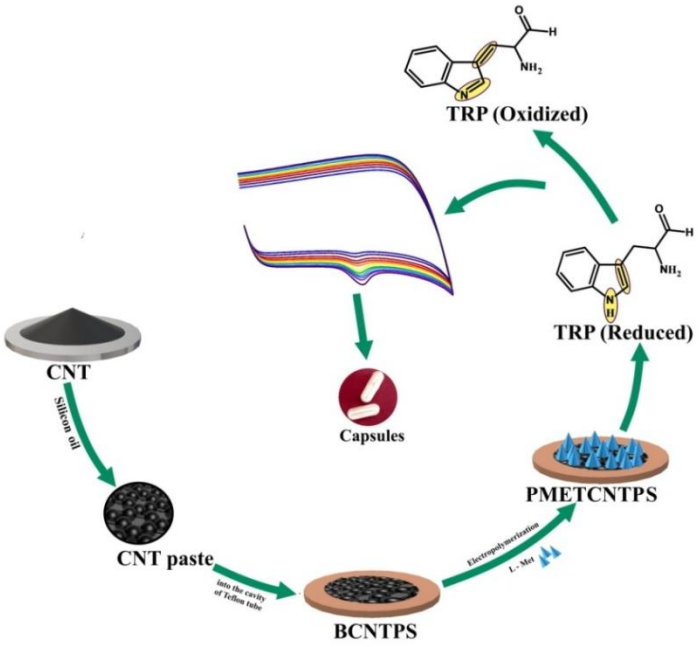


Chapter 5B: Poly- (Methionine) modified Carbon Nanotube Sensor for the sensitive and selective determination of L-Tryptophan

(**Journal of Electrochemical Science and Engineering,** 10, 2020, 305-315. **Cite Score: 2.3**)

This chapter deliberates the electrochemically initiated catalytic oxidation of amino acid L-tryptophan (L-TRP) in phosphate buffer solution has been scrutinized using highly conductive poly-(methionine) modified carbon nanotube paste sensor (PMETCNTPS) through CV

technique. Compared to the bare carbon nanotube paste sensor (BCNTPS), PMETCNTPS exhibited a quantifiable current signal by CV method. PMETCNTPS was found sensitive to L-TRP concentrations within the linear segment of detection range 1.5×10^{-5}- 8.0×10^{-5} M. By employing the calibration plot, the detection limit was determined as 6.99×10^{-7} M. In addition, PMETCNTPS was successfully exploited and validated in determining L-TRP in the pharmaceutical supplement.

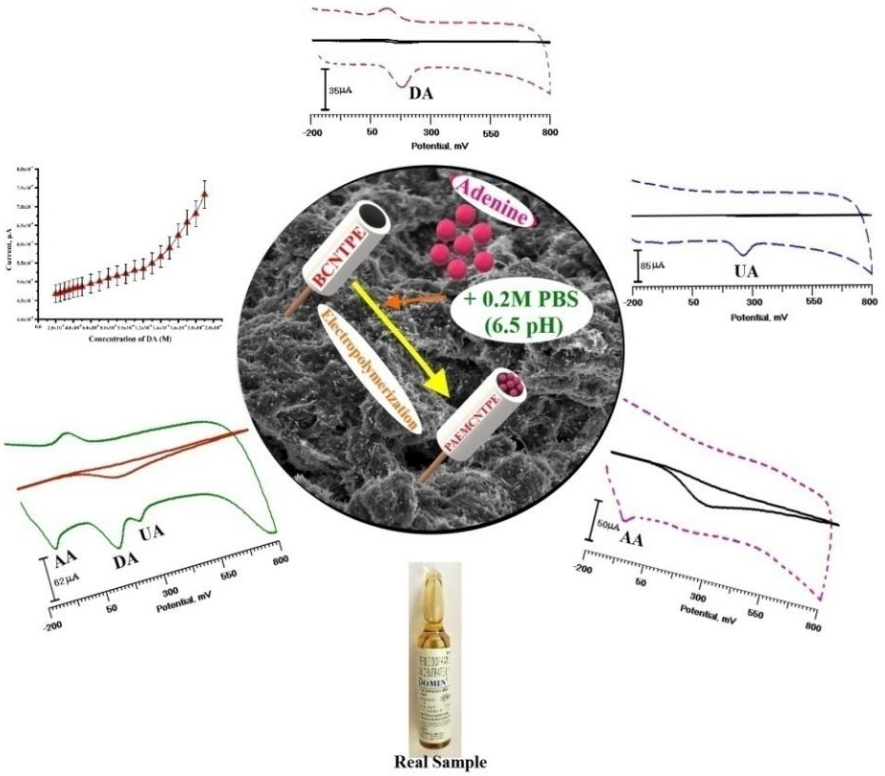


Chapter 6: Electrocatalytic Analysis of Dopamine, Uric Acid and Ascorbic Acid at Polyadenine modified Carbon Nanotube Paste Electrode: A Cyclic Voltammetric Study

(**Analytical & Bioanalytical Electrochemistry,** 11, 2019, 742-756. **Cite Score: 1.38**)

This chapter offers the details about the Polyadenine film modified carbon nanotube paste electrode (PAEMCNTPE), prepared by electropolymerization of adenine on a carbon nanotube paste electrode, and applied for the sensitive and selective analysis of dopamine (DA), Uric acid

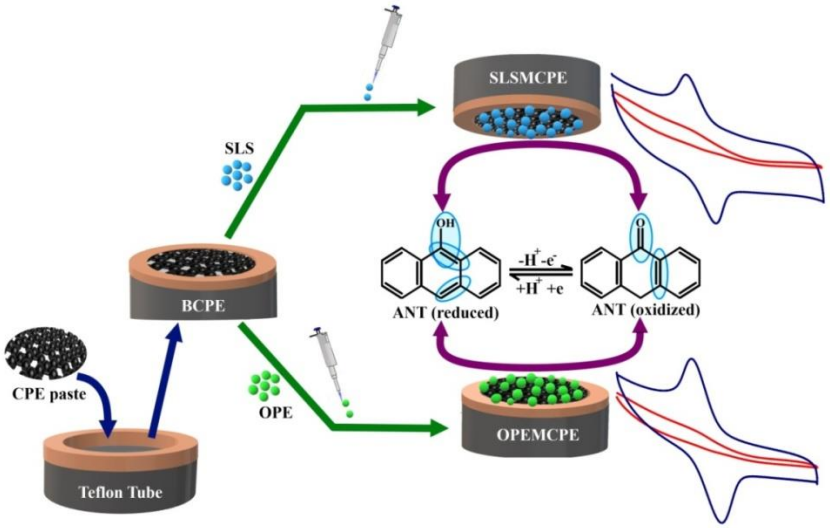
(UA) and Ascorbic acid (AA) based on cyclic voltammetric technique. The polyadenine modified carbon nanotube paste electrode has presented with an impressive electrocatalytic activity towards oxidation of DA, UA, and AA in the presence of supporting electrolyte, 0.2 M PBS pH 6.5. The surface of fabricated sensor displayed with a permselective layer with transducing, anti- interfering and anti-fouling properties followed by solving the overlapped peaks of DA, AA and UA obtained from the conventional electrode by presenting with distinct three anodic peaks. The result of this electrochemical sensor displayed with excellent sensitivity, selectivity, reproducibility, repeatability and highly stable. The detection limit for DA was 6.7 × 10^{-7} M. Further; this fabricated electrode was carried out for the quantification of DA in the real sample.



Chapter 7: Surfactant Modified Electrochemical Sensor for Determination of Anthrone – A Cyclic Voltammetry

(**Materials Science for Energy Technologies,** 2, 2019, 408-416. **Cite score: 12.0**)

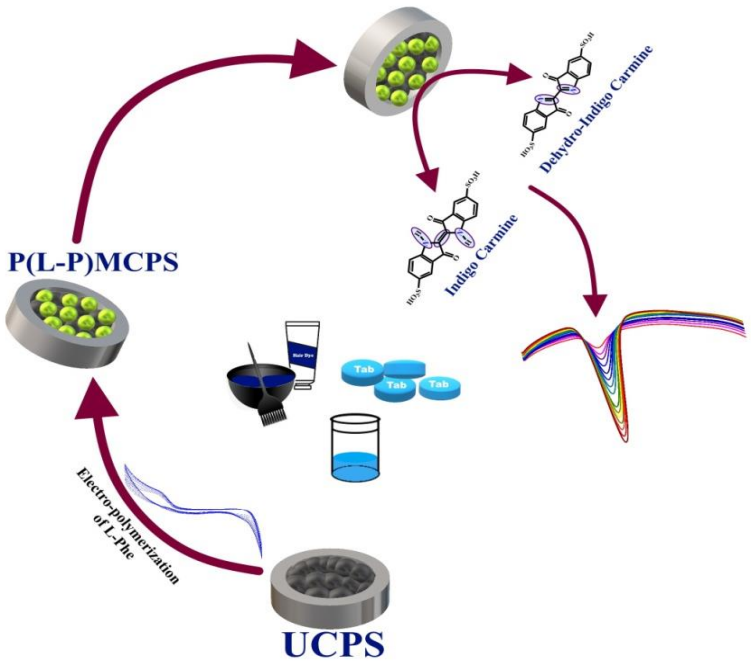
This Chapter discusses about the two promising electrochemical sensor constructed using carbon paste electrode modified with Octyl phenol ethoxylate surfactant (OPEMCPE) and carbon paste electrode modified with Sodium lauryl sulfate (SLSMCPE). The electrochemical characterization of Anthrone (ANT) was studied at the surface of OPEMCPE with supporting electrolyte of pH 7.0 in 0.1M phosphate buffer (PBS) and also at the surface of SLSMCPE with supporting electrolyte of pH 7.5 in 0.1M PBS by using CV and DPV. The OPEMCPE and SLSMCPE exhibited an efficient electrocatalytic activity towards ANT than the bare carbon paste electrode (BCPE). The characterization of both the electrodes is done by FE-SEM and EDX for SLSMCPE. The detection limit and limit of quantification of ANT employed in CV at the surface of OPEMCPE were 18.8×10^{-7} M and 6.27×10^{-6} M and at the surface of SLSMCPE were 10.6×10^{-7} and 3.53×10^{-6}. Moreover, tailored electrode offers high sensitivity, highly stable, good conductivity, transducing, biocompatibility, reliable to resistant electrode fouling and good reproducibility.



Chapter 8: Application of a rapid and cost-effective voltammetric sensor for the determination of hazardous azo-dye Indigo Carmine

(Communicated to **ACS Omega, I.F: 4.132**)

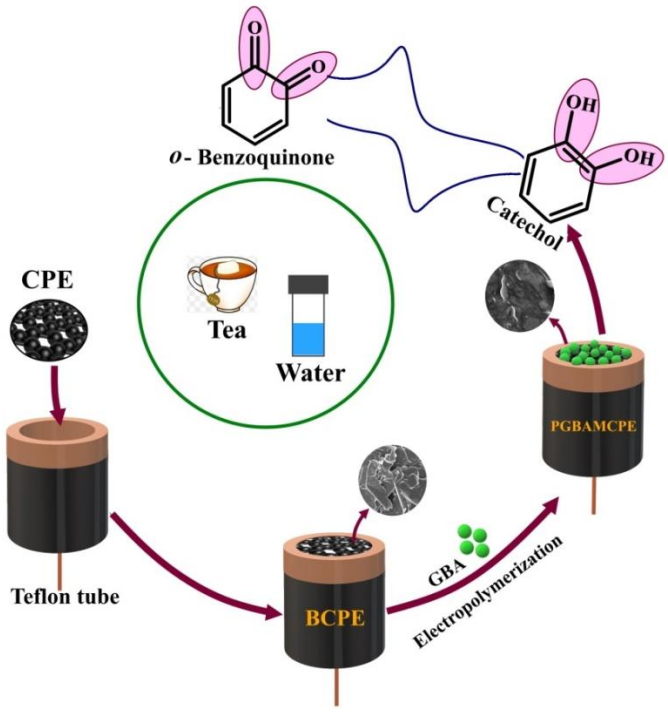
Indigo carmine (IC) is a hazardous synthetic dye and toxic to the humans but still it has been extremely employed in various industries. In convenient to this, a reliable method of fabricated Poly (L-phenylalanine) modified carbon paste sensor (P(L-P)MCPS) for the study of electrochemical oxidation of IC is reported here. The fabrication was done by simple electro-polymerization technique. The biocompatible proposed sensor is characterized by FE-SEM, EIS, and CV studies. DPV were utilized to assess the concentration of IC. The DPV studies display a linear range of 0.1 µM to 5 µM with lower detection limit of 1.8×10^{-8} M. The applicability of P(L-P)MCPS has been effectively verified in the analysis of real samples like hair dye powder, water and pharmaceutical tablet.



Chapter 9: A Highly Selective and Sensitive Voltammetric Method for the Detection of Catechol in Tea and Water samples using Poly (Gibberllic acid) modified carbon paste electrode

(**ACS Omega,** 7, 2022, 24679-24687. **I.F: 4.132**)

Despite of having wide range of applications of CC in agrochemical, petrochemical, textile, cosmetics and pharmaceutical industries, its exposure to the environment lead to health issues as it is carcinogenic. This increased the concern over the risk of exposure level of CC in the environment and has become critical in monitoring its level. In this work, we report the fabrication of Poly- Gibberellic acid modified carbon paste electrode (PGBAMCPE) to be simple, cost-effectively viable and an effective electrochemical electrode for the determination of CC. This was synthesized by simple electro-polymerization method by CV technique. The electrodes were characterized by FE-SEM, EDX and EIS. Compared to BCPE the sensitivity for CC fortified at PGBAMCPE at both CV and DPV. We succeeded attaining lower detection limit (DL) of 0.57 µM by DPV method. The developed electrode was highly conductive, transducing and achieved to be highly selective with anti-interfering properties by determining CC with hydroquinone (HQ) simultaneously. The applicability of electrode was confirmed in detecting CC in tea and water samples with good recoveries. This substantiates PGBAMCPE is promising and consistent for rapid monitoring of CC contaminated area and clinical diagnosis.

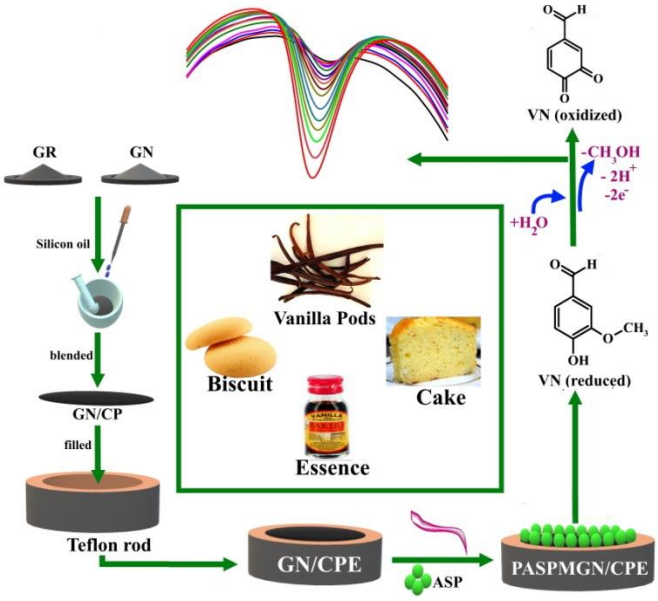


Chapter 10: Rapid Voltammetric Approach for the Sensing of Food Additive Vanillin on the surface of Poly (Aspartic Acid) modified Graphene and Graphite composite Paste Sensor

(Communicated to **ChemistrySelect, I.F: 2.3**)

VLN is generally used in bakery food products as an aroma enhancer and flavoring agent. Hence it is important to develop a powerful and rapid tool to monitor the concentration of VLN level in concerning to the food safety. In this paper, simple sensor was proposed by electropolymerized Aspartic acid modified on Graphene and Graphite composite paste electrode PASPMGN/CPE for the detection of VLN by DPV. PASPMGN/CPE ranked to have high electrocatalytic kinetics towards electro-oxidation of VLN, in optimized condition. The electrochemical process of VLN portrayed to be irreversible and adsorption-controlled kinetics by CV method. The surface features were studied using FE-SEM, EDX, EIS and CV. From DPV

results, the oxidative peak current shown with linear growth towards the concentration of VLN ranging from 1 µM to 2.0 µM with LOD and LOQ of 4.85 µM and 16.2 µM. The modified sensor attained to be highly selective with common possible interferents. PASPMGN/CPE was efficient in detecting VLN in vanilla pods, essence and bakery products samples.



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1. **Nambudumada S. Prinith,** Jamballi G. Manjunatha, Girish Tigari, Zeid A. ALOthman, Amer M. Alanazi and Anup Pandith, Mechanistic Insights into the Voltammetric Determination of Riboflavin at Poly (Serine) Modified Graphite and Carbon Nanotube Composite Paste Electrode, **ChemistrySelect,** 6, 2021, 10746-10757, **DOI** - 10.1002/slct.202103184, **ISSN-** 2365-6549**, I.F 2.3.**

2. **Nambudumada S. Prinith,** Jamballi G. Manjunatha and Nagarajappa Hareesha, Electrochemical validation of L-tyrosine with dopamine using composite surfactant modified carbon nanotube electrode, **Journal of the Iranian Chemical Society,** 18, 2021, 3493-3503, **DOI** - 10.1007/s13738-021-02283-z, **ISSN-** 1735-207X**, I.F 2.27.**

3. **Nambudumada S. Prinith,** Jamballi G. Manjunatha, Electrochemical analysis of L-Tryptophan at highly sensitive poly (Glycine) modified carbon nanotube paste sensor, **Materials Research Innovations,** 26, 2022, 134-143, **DOI** - 10.1080/14328917.2021.1906560, **ISSN**-1432-8917**, Cite score 4.0.**

4. **Nambudumada S. Prinith,** Jamballi G. Manjunatha, Polymethionine modified carbon nanotube sensor for sensitive and selective determination of L-tryptophan, **Journal of Electrochemical Science and Engineering**, 10, 2020, 305-315, **DOI** - 10.5599/jese.774, **ISSN**-1847-9286, **Cite score 2.3.**

5. **Nambudumada S. Prinith,** Jamballi G. Manjunatha and Chenthattil Raril**,** Electrocatalytic Analysis of Dopamine, Uric Acid and Ascorbic Acid at Polyadenine modified Carbon

Nanotube Paste Electrode: A Cyclic Voltammetric Study, **Analytical & Bioanalytical Electrochemistry,** 11, 2019, 742-756, **ISSN**-2008-4226, **Cite score 1.38.**

6. **N.S. Prinith,** J. G. Manjunatha, Surfactant Modified Electrochemical Sensor for Determination of Anthrone – A Cyclic Voltammetry, **Materials Science for Energy Technologies,** 2, 2019, 408–416, **DOI** - 10.1016/j.mset.2019.05.004, **ISSN**-2589-2991, **Cite score 12.0.**

7. **Nambudumada S. Prinith,** J. G. Manjunatha, Abdullah A Al-Kahtani, Ammar M. Tighezza and Mika Sillanpää, Highly Selective and Sensitive Voltammetric Method for the Detection of Catechol in Tea and Water Samples Using Poly (gibberellic acid)- Modified Carbon Paste Electrode, **ACS Omega,** 7 (2022) 24679-24687, DOI - 10.1021/acsomega.2c02553, **ISSN**-2470-1343, **I.F: 4.132**

8. J. G. Manjunatha, C. Raril, **N. S. Prinith**, P. A. Pushpanjali, M. M. Charithra, Girish Tigari, N. Hareesha, Edwin S D'Souza, B. M. Amrutha, Fabrication, characterization and application of poly (acriflavine) modified carbon nanotube paste electrode for the electrochemical determination of catechol, **Handbook of Nanomaterials for Sensing Applications,** 2021, 105-117. **DOI** - 10.1016/B978-0-12-820783-3.00022-1.

9. N. Hareesha, J. G. Manjunatha, B. M. Amrutha, P. A. Pushpanjali, M. M. Charithra and **N. Prinith Subbaiah**, Electrochemical Analysis of Indigo Carmine in Food and Water Samples Using a Poly(Glutamic Acid) Layered Multi-walled Carbon Nanotube Paste Electrode, **Journal of Electronic Materials,** 50, 2021, 1230-1238, **DOI** -10.1007/s11664-020-08616-7, **ISSN-** 0361-5235, **I.F: 2.047.**

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1. N.S. Prinith, J. G. Manjunatha, Sensitive Voltammetric Determination of L-Tryptophan at Polymer Modified Carbon Nanotube Paste Electrode. International conference on "Electrochemistry in Industry, Health and Environment" organized by the Indian Society of ElectroAnalytical Chemistry, Bhabha Atomic Research Centre, Mumbai from 21st to 25th January, 2020

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3. N.S. Prinith, J. G. Manjunatha, C. Raril, Simultaneous Analysis of Dopamine, Uric Acid and Ascorbic Acid at Polyadenine Modified Carbon Nanotube Paste Electrode – A Cyclic

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Research Scholar
(Prinith Subbaiah N.)

Research Guide
(Dr. J.G. Manjunatha)

Analytical Chemistry

Mechanistic Insights into the Voltammetric Determination of Riboflavin at Poly (Serine) Modified Graphite and Carbon Nanotube Composite Paste Electrode

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Intense present work is directed on the fabrication and application of Poly (serine) modified graphite carbon nanotube composite paste electrode (PSR/CNTPE) for determining the Riboflavin (RF). The surface qualities of the projected sensor were observed by Field Emission Scanning Electron Microscopy (FE-SEM) and the conductivity by Electrochemical Impedance Spectroscopy (EIS) method. The electrochemical redox activity of the PSR/CNTPE to RF was investigated through Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV). Outcomes displays that Poly (serine) in CNTPE enhanced the catalytic performance of the electrode towards the redox reaction of RF. The voltammetric response of PSR/CNTPE exhibited linear dependence for extended concentration range of RF from 6 μM to 50 μM with lower detection limit of 3.4×10^{-8} M.The PSR/CNTPE revealed to be reproducible, highly stable and successfully validated for the pharmaceutical, beverage and milk samples. The fabricated electrode was conducive and displayed two well-separated oxidation signals for the solution containing two vitamins RF and Folic Acid (FA). The projected sensor is an adequate candidate for electrochemical sensing of RF.

1. Introduction

Vitamins have the chief role in the metabolism and essential as diet for the growth of body tissues and nutrition in humans. Vitamin B_2, namely Riboflavin is a water-soluble candidate of the vitamin B clan. In the body, RF is mostly found to be the basic factor of two coenzymes that is, Flavin Adenine Dinucleotide (FAD) and Flavin Mono Nucleotide (FMN).[1,2] They have a predominant role for the mitochondrial energy production carried out by electron transport chain, oxidation of fatty acids, metabolism of niacin, folate and pyridoxine, catabolism of dopamine and serotonin, activation of glutathione reductase and thioredoxin reductase.[3–5] Therefore, its need is important for human health as it is not synthesized within the body, so RF is ingested by ingestion of food like meat, fatty fish, egg, particular fruits and vegetables mainly dark green vegetables.[6] Pregnancy women are insisted to have higher amount of RF as it passes through placenta.[7] An inadequate concentration level of RF in human body put forth to various health complications such as ariboflavinosis, oxidative stress, and cataract.[8–10] Folic acid is another water-soluble vitamin B, generally known as vitamin B_9 or folacin. Like RF, FA also cannot be synthesized in the human body; it must be consumed by intake of food like asparagus, green leafy vegetables, legumes and oranges. It is necessary for its role in metabolizing the amino acid for the production of deoxyribonucleic acid and ribonucleic acid. The scarce of FA in the body can initiate the following health diseases like anaemia, cardiovascular, cancer and alzheimer's. FA can prevent neural tube birth defects in newborns.[11,12]

As of now, many analytical methods like Ultra-violet spectroscopy, High-performance liquid chromatography (HPLC), Chemiluminescence, Mass spectrometry, Spectrophotometry, ultra-high-performance liquid chromatography / liquid chromatography-mass spectrometry (UHPLC/LC-MS), Surface Plasmon Resonance have been involved for the determination of RF.[8,13,14] In account to these methods, they have their own merits and demerits. These techniques are chiefly taking more time for the determination of various bioactive molecules; the instruments are expensive, complications in sample preparation and processing. At present days, the electrochemical techniques have notched up for their unique features in holding low cost equipments, simple, and easy procedures and processing, high sensitivity, reliable and convenient for determination of biomolecules.[15,16]

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ORIGINAL PAPER

Electrochemical validation of L-tyrosine with dopamine using composite surfactant modified carbon nanotube electrode

Nambudumada S. Prinith[1] · **Jamballi G. Manjunatha**[1] · **Nagarajappa Hareesha**[1]

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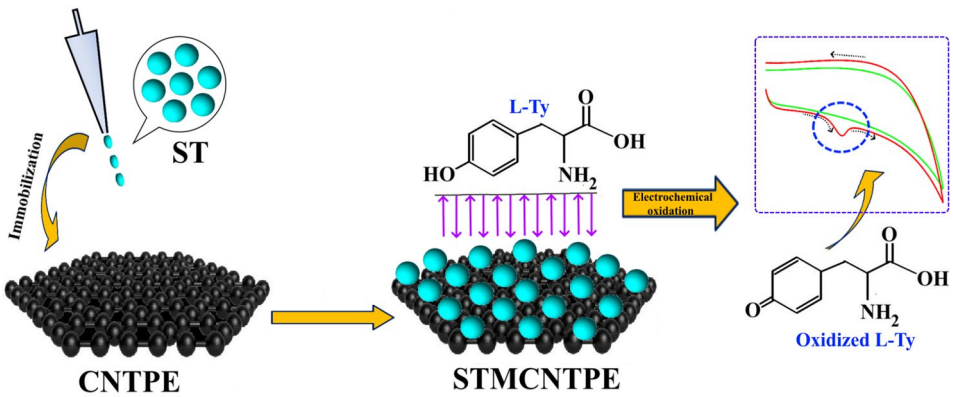
Abstract

Herein, for the first time, we employed sodium lauryl sulfate and Triton X-100 composite surfactants immobilized on the carbon nanotube paste electrode (STMCNTPE) as an electrochemical sensor for the electro-catalytic oxidation of L-tyrosine (L-Ty) and dopamine (DP) through cyclic voltammetry. The STMCNTPE exhibited a robust enhancement impact on the oxidation of L-Ty with enhanced current signal compared to other electrodes. In ideal conditions, various parameters were studied such as pH value, concentrations of surfactants, different ranges of sweep rates, the concentration of an analyte, simultaneous study, and the interference analysis. The proposed sensing film unveiled with a detection limit 3.75×10^{-7} M and quantification limit 1.22×10^{-6} M for a wide linear range. The STMCNTPE revealed with remarkable sensitivity, selectivity, long-term stability, good reproducibility and repeatability, biocompatible, enhanced electrode fouling resistance, and anti-interference. Finally, the sensing film STMCNTPE carried out successfully for the analysis of L-Ty in cow's milk and pharmaceutical drug.

Graphic abstract

The novel electrode was developed by immobilization of composite surfactant ST was modified on carbon nanotube paste electrode (STMCNTPE) was utilized for validating the electrochemical oxidation of L-tyrosine using CV technique. The single quantified peak revealed to be irreversible carrying one electron and one proton transfer. The STMCNTPE was further studied simultaneously with DP. The proposed sensor was successfully validated on milk sample and pharmaceutical drug analysis. The STMCNTPE presented with good stability, reproducible and sensitive with low limit of detection 3.75×10^{-7}.



Keywords Mixed surfactants · Carbon nanotube electrode · L-tyrosine · Dopamine · Cyclic voltammetry · Electrochemical sensor

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RESEARCH ARTICLE

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Electrochemical analysis of L-Tryptophan at highly sensitive poly(Glycine) modified carbon nanotube paste sensor

Nambudumada S. Prinitha and Jamballi G Manjunatha

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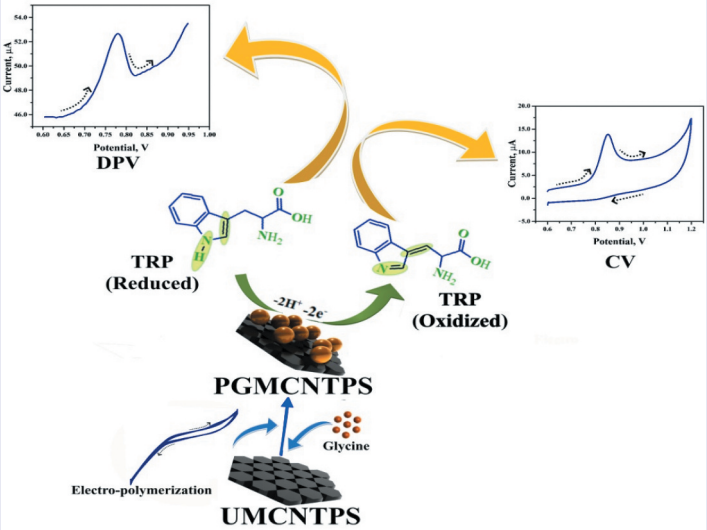
ABSTRACT

In the present work, we developed poly(Glycine) modified carbon nanotube paste electrode (PGMCNTPE) as a biosensor for eliciting the electrooxidation of L-Tryptophan (TRP). The surface of the sensors was characterised by Field emission scanning electron microscopy (FE-SEM) and Electrochemical impedence spectroscopy (EIS). The analysis of TRP was succeeded at the surface of PGMCNTPE for their high electrical conductivity and electrostatic interaction, that amplified the oxidation peak current by 8 fold in cyclic voltammetry (CV) and by 12 fold in differential pulse voltammetry (DPV) as compared to unmodified electrode. The activity of sensor on TRP was manifested to be irreversible reaction proceeding with the transfer of $2e^-$ and $2H^+$ and adsorption controlled. Under the optimal state, it was noteworthy that the execution of the sensor revealed to have a low detection limit of 0.42 µM on a broad linear range of 20 µM to 100 µM. Lastly, the determination of TRP was exploited successfully in the pharmaceutical supplement.



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L-tryptophan; voltammetry; poly(glycine); carbon nanotube paste sensor; electrochemical impedance study

INTRODUCTION

Amino acids have a predominant role in the biotic life as it is the key figure for the synthesis of proteins, enzymes, and intermediates in the metabolic pathways and for the generation of adenosine triphosphate. Hence, the analysis of amino acids is seemed to be engrossed by the researchers.

TRP is an essential α-amino acid having the derivative of alanine possessing with a heterocyclic substituent indole located on the β-carbon. Despite, from the synthesis of proteins and for preserving the nitrogen balance, it also acts as the precursor for the following biomolecules such as niacin, melatonin, tryptamine, kynurenic acid, serotonin, quinolinic acid, and nicotinamide adenine dinucleotide [1–3]. The benefits of the intake of TRP can ward off from the effect of the growth of children, chronic insomnia, depression, and pellagra. Therefore, it is necessary for the diet of kids and adult humans [4,5]. The sources of TRP can be obtained from various foods like milk, bananas, dried prunes, oats, peanuts, bread, cheese, chicken, tuna fish, chocolates, turkey and pharmaceutical supplements [6]. Even if the intake of TRP is at higher concentration can lead to eosinophilia-myalgia syndrome and if it is not completely metabolised chances of the formation of toxic products in the brain arising to delusions and hallucinations [7,8]. From these, TRP can be coined to have two faces as the coin. Thenceforth, this stimulates an upsurge of interest in developing the methods for determining the TRP and monitoring their levels in health and clinical diagnosis.

Several methods were performed for the quantitative analysis of TRP like fluorometric, chemiluminescence, spectroscopy, high-performance liquid chromatography, capillary electrophoresis [9–13] all of these methods hold high-cost instrumentation, cumbersome and demand of pre-treatment, sophisticated in manipulating the procedures and time-

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Original scientific paper

Polymethionine modified carbon nanotube sensor for sensitive and selective determination of L-tryptophan

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Abstract

The electrochemically initiated catalytic oxidation of amino acid L-tryptophan (L-TPN) in phosphate buffer solution has been scrutinized using highly conductive polymethionine modified carbon nanotube paste sensor (PMETCNTPS) through cyclic voltammetry (CV) technique. Compared to the bare carbon nanotube paste sensor (BCNTPS), PMETCNTPS exhibited a quantifiable current signal by CV method. PMETCNTPS was found sensitive to L-TPN concentrations within the linear segment of detection range 1.5 - 8.0×10^{-5} M. By employing the calibration plot, the detection limit was determined as 6.99×10^{-7} M. In addition, PMETCNTPS was successfully exploited and validated in determining L-TPN in the pharmaceutical supplement.

Keywords

Electrochemical sensor; tryptophan; electropolymerization; cyclic voltammetry.

Introduction

Amino acids play a substantial role in biotic life and are necessary for human beings as a source of energy and for building up the proteins. Tryptophan (L-TPN) is an essential proteinogenic amino acid responsible for serving as a precursor for the neurotransmitter drug serotonin, melatonin hormone and nicotinic acid [1,2]. Therefore, the intake of L-TPN is important for humans because it has low storage in tissues and total concentration of L-TPN in the body is the least compared to all other amino acids. The small quantity of L-TPN which is necessary for human nutrition can be supplied from foods such as bananas, oats, tuna fish, milk, chocolates, dried prunes, chicken, peanuts, bread, cheese, turkey, supplements, and pharmaceutical formulations [3]. L-TPN has a major impact on the brain, since if not properly metabolized, a waste toxic product would be formed, leading to delusions and hallucinations [4]. It has already been pointed out that depletion of L-TPN levels is accompanied by weight gain, affecting the growth of kids, anxiety, chronic

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Full Paper

Electrocatalytic Analysis of Dopamine, Uric Acid and Ascorbic Acid at Poly(Adenine) Modified Carbon Nanotube Paste Electrode: A Cyclic Voltammetric Study

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Abstract- In this work, Poly (adenine) film modified carbon nanotube paste electrode (PAEMCNTPE), prepared by electropolymerization of adenine on a carbon nanotube paste electrode, applied for the sensitive and selective analysis of dopamine (DA), Uric acid (UA) and Ascorbic acid (AA) based on cyclic voltammetric technique. The polyadenine modified carbon nanotube paste electrode has presented with an impressive electrocatalytic activity towards oxidation of DA, UA, and AA in the presence of supporting electrolyte, 0.2 M PBS pH 6.5. The surface of fabricated sensor displayed with a permselective layer with transducing, anti- interfering and anti-fouling properties followed by solving the overlapped peaks of DA, AA and UA obtained from the conventional electrode by presenting with distinct three anodic peaks. The result of this electrochemical sensor displayed with excellent sensitivity, selectivity, reproducibility, repeatability and highly stable. The detection limit for DA was 6.7×10^{-7} M. Further; this fabricated electrode was carried out for the quantification of DA in the real sample.

Keywords- Carbon nanotube electrode, Polyadenine, Electropolymerization, Dopamine, Cyclic Voltammetry

1. INTRODUCTION

DA, is often known as 3, 4-dihydroxyphenethylamine. It's an organic compound belonging to the families of catecholamine and plays a crucial role in the brain as well as the body, functioning as a neurotransmitter and neuromodulator in the mammalian central nervous

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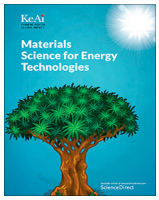

Surfactant modified electrochemical sensor for determination of Anthrone – A cyclic voltammetry

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ABSTRACT

The two promising electrochemical sensor constructed using carbon paste electrode modified with Octyl phenol ethoxylate surfactant (OPEMCPE) and carbon paste electrode modified with Sodium lauryl sulfate (SLSMCPE). The electrochemical characterization of Anthrone (ANT) was studied at the surface of OPEMCPE with supporting electrolyte of pH 7.0 in 0.1 M phosphate buffer (PBS) and also at the surface of SLSMCPE with supporting electrolyte of pH 7.5 in 0.1 M PBS by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The OPEMCPE and SLSMCPE exhibited an efficient electrocatalytic activity towards ANT than the bare carbon paste electrode (BCPE). The characterization of both the electrodes are done by FE-SEM and EDX for SLSMCPE. The detection limit and limit of quantification of ANT employed in CV at the surface of OPEMCPE were 18.8×10^{-7} M and 6.27×10^{-6} M and at the surface of SLSMCPE were 10.6×10^{-7} M and 3.53×10^{-6} M. Moreover, tailored electrode offers high sensitivity, highly stable, good conductivity, transducing, biocompatibility, reliable to resistant electrode fouling and good reproducibility.

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1. Introduction

9[10H]-Anthracenone is commonly known as Anthrone (ANT) which is an organic compound belonging to a polycyclic aromatic hydrocarbon. It's widely applied in the colorimetric assay of carbohydrates and cellulose [1,2]. It acts as an antipsoriatic agent and laxative for the stimulation of motion in the colon [3,4]. It exhibits a potent antioxidant activity as it has a property of strong reducing power and scavenging influence on hydroxyl radicals [5]. ANT is toxic to the environment as a pollutant due to the photooxidation process of Anthrone releasing the reactive oxygen species mainly singlet oxygen ($^1O_2$) responsible for pollutant and tested to be most toxic to the mammalian cells [6,7]. In atmosphere Anthrone exists in both vapor and particulate phases. The impact of this particulate on human may cause irritation or burning in the respiratory tract and long term exposure may lead to acute lung injury, pulmonary edema, bronchospasm. The ANT undergoes tautomerism readily to yield Anthranol (Scheme1) [8]. As the polyaromatic hydrocarbons are more toxic to the environment and studied that Anthrones are more prone to be toxic compared to the anthraquinones [5] and found in some cities as it is a victim of toxic [6,9] The analytical methods implemented on ANT are less, few are Laser Flash [8], Spectrophotometric [10] and electroanalytical mode [11].

In the area of the electrochemical field, the work on surfactant has emerged extensively for its unique property as it is an amphiphilic molecule containing hydrophobic head and hydrophilic tail [12–16]. Octyl phenol ethoxylate commonly known as Triton X-100 which is a non-ionic surfactant and has the property of behaving as structure directing agent. [17] and Sodium Lauryl Sulfate commonly known as Sodium dodecyl sulfate which is an anionic surfactant. Many research works have been reported on surfactants for its easy fabrication, to improve the characteristics of electrode-solution interface, can decrease the electrode fouling, large surface area, specific porosity and also subsequently enhance the limit of detection of few bioactive moieties [18–30].

In our current analysis, we used two types of surfactant-modified electrodes OPEMCPE and SLSMCPE along with bare carbon paste electrode BCPE for the study of the voltammetric response of ANT. As per to our knowledge the electroanalytical work on ANT is less. The core of this study was to analyze the

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Article

Highly Selective and Sensitive Voltammetric Method for the Detection of Catechol in Tea and Water Samples Using Poly(gibberellic acid)-Modified Carbon Paste Electrode

Nambudumada S. Prinith, J. G. Manjunatha,* Abdullah A. Al-Kahtani, Ammar M. Tighezza, and Mika Sillanpää

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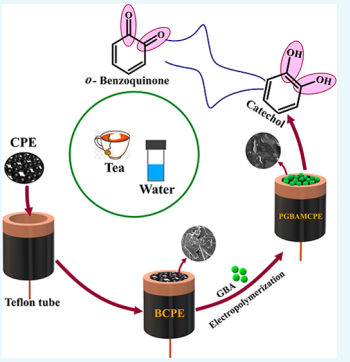
ABSTRACT: Despite the wide range of applications of catechol (CC) in agrochemical, petrochemical, textile, cosmetics, and pharmaceutical industries, its exposure to the environment leads to health issues as it is carcinogenic. This increased the concern over the risk of exposure level of CC in the environment, and monitoring its level has become critical. In this work, we report the fabrication of poly-gibberellic acid-modified carbon paste electrode (PGBAMCPE) to be a simple, viable, and effective electrochemical electrode for the determination of CC. This was synthesized by a simple electropolymerization method by the cyclic voltammetry (CV) technique. The electrodes were characterized by field emission electron microscopy, energy-dispersive X-ray spectroscopy, and electrochemical impedance spectroscopy. Compared to the bare carbon paste electrode, the sensitivity for CC fortified at PGBAMCPE in both CV and differential pulse voltammetry (DPV). We succeeded attaining a lower detection limit of 0.57 μM by the DPV method. The developed electrode was observed to be highly conductive, transducing, stable, and reproducible and was highly selective with anti-interfering properties from the determination of CC with hydroquinone simultaneously. The applicability of the electrode was confirmed from the detection CC in tea and water samples with good recoveries. This substantiates that PGBAMCPE is promising and consistent for the rapid monitoring of CC-contaminated area and clinical diagnosis.



1. INTRODUCTION

Strict enforcement measures are necessary in regulating the exposure level of organic pollutants to prevent the risk of environmental and human health.[1−4] Therefore, there is a requisite to delve on the exposure level of these toxic wastes. The organic pollutants containing phenolic derivatives are the major threat to the environment. Such organic compounds arise from agrochemical, petroleum, textile, and pharmaceutical industries. Catechol (CC) (1,2-dihydroxy benzenediols) is one of the ortho-isomers of the three benzenediols. It is an acute toxic organic phenol compound, and on contact with human skin, it leads to eczematous dermatitis and is also carcinogenic.[5,6] CC is greatly produced due to anthropogenic activities like processing of coal tar, manufacturing of insecticides, production of perfumes and drugs, waste incineration plants, and so forth.[7] Small amounts of CC are predominantly found in naturally occurring plants like pine, tea, oak, and so forth and fruits and vegetables like apples, potatoes, onions, and so forth.[8] A larger dosage of CC affects the central nervous system. Therefore, there is an upsurge of importance in governing CC environmentally and clinically.

After going through various literature reports, the quantitative analysis of CC was carried out by utilizing innumerable sophisticated methods, such as HPLC, GC−mass spectrometry, flow injection chemiluminescence, fluorescence, and so forth,[9−12] which require expensive apparatus, pretreatments, trained personnel to handle and operate the apparatus, and is a time-consuming process.[13] Hence, the applications of the aforementioned methods were greatly prevented in the rapid detection of target analytes. In contrast to the approach of complicated methods, voltammetry has achieved more attention for its intrinsic merits of economical apparatus, sensitivity, simple and smooth operation, portability, and immediate on-site response of target analytes disclosing the charge-transfer abilities.[14−16] As CC is electrochemically active, its analytical reaction has been improvized by numerous newly developed modified electrochemical sensors. As a result, these studies support in understanding the electrochemical activity of the target analyte. Further, it helps in the quantification of trace amounts of target analytes present in the biological samples.

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Convener, EIHE 2020

Gyanam Vijnanam Cha Bhaktisahitam

RAMAIAH
College of Arts, Science & Commerce

CERTIFICATE
of Participation

24 - 26 October 2019

This is to certify that

Dr/Prof/Mr/Mrs/Ms PRINITH SUBBAIAH NAMBUDUMADA

has participated as delegate and presented an Oral Paper/Poster/Keynote Address/Invited Lecture/Chaired a Scientific Session/Volunteered in the 1st International Conference on Life, Chemical, and Health Sciences (ICLCHS) Organized by Department of Life Sciences Ramaiah College of Arts, Science & Commerce in collaboration with Karnataka Science and Technology Academy (KSTA), Department of IT, BT, and Science & Technology, Government of Karnataka (GoK).

Dr Nagagireesh Bojanala
Dean of Sciences & Head of Research
College of Arts, Science & Commerce

Dr Nagaratna A
Principal,
College of Arts, Science & Commerce

Dr A M Ramesh
Chief Executive Officer
KSTA

Dr H. Honne Gowda
Special Secretary (Technical)
Department of IT, BT and Science & Technology
Govt. of Karnataka

Mangalore University
Indian Association of Biomedical Scientists (IABMS)

39th IABMS 2018

39th Annual Summit of Indian Association of Biomedical Scientists (IABMS)
International Conference on
"Current concepts on the role of Indian medicine and phytoceuticals in maintenance of health"

Certificate

This is to certify that Prinith Subbaiah N [Mangalore University] *has participated & presented ~~Oral~~/Poster/ as a Delegate in the International Conference held from 15 - 17th November 2018, organised by the Department of Studies & Research in Biochemistry, Mangalore University, Jnana Kaveri, Post Graduate Centre, Chikka Aluvara, Kodagu, Karnataka, India.*

Prof. A. M. Khan
Registrar
Mangalore University

Prof. T. Thirunalasundari
President
IABMS

Prof. S. Karthikeyan
General Secretary
IABMS

Prof. Manjula Shantaram
Organizing Secretary
39th IABMS Conference 2018

Mangalore University

FIELD MARSHAL K.M.CARIAPPA COLLEGE

(A Constituent College of Mangalore University)

(Recognised by UGC as College with Potential for Excellence)

National Level Conference

(Under CPE Programme)

CERTIFICATE

This is to certify that Ms. Prinith Subbaiah N. *of* F.M.K.M.C. College, Madikeri *has participated as* ~~Chair person~~ / ~~Resource person~~ / ~~Oral Presenter~~ / Poster Presenter / ~~Delegate~~ *in the National Level Conference on "Recent Advances in Material Science" held on 5th February 2019 organised by the Department of Chemistry, Field Marshal K. M. Cariappa College, Madikeri.*

J. G. Manjunatha

Dr. Manjunatha J. G.
Convener

Dr. T. D. Thimmaiah
Principal

Mangalore University

FIELD MARSHAL K.M.CARIAPPA COLLEGE

(A Constituent College of Mangalore University)

(Recognised by UGC as College with Potential for Excellence)

National Conference

CERTIFICATE

This is to certify that Prinith Subbaiah N *of* F M K M C College, Madikeri *has participated as* ~~*Chair person*~~ */* ~~*Resource person*~~ */* ~~*Oral Presenter*~~ */ Poster Presenter /* ~~*Delegate*~~ *in the National Level Conference on "Recent Novel Approaches in Chemical Sciences" held on 12th February 2020 organised by the Department of Chemistry, Field Marshal K.M. Cariappa College, Madikeri.*

J. G. Manjunatha

Dr. Manjunatha J. G.
Convener

Dr. C Jagath Thimmaiah
Principal